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ABSTRACTS

TECHNOLOGY TRANSFER CONFERENCE No.5

November 27 & 28 , 1984

This two day conference features papers dealing with research aspects of air pollution, water treatment, liquid and solid waste disposal, as well as analytical and instrumental method development. These topics will be presented in two concurrent sessions.

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**HAZARDOUS CONTAMINANTS
AND STANDARDS BRANCH**
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PREFACE

This booklet was prepared to provide the reader with the abstracts of those papers presented at Technology Transfer Conference No. 5 held on November 27 and 28, 1984 and organized by the Ontario Ministry of the Environment.

For more details, the reader is referred to the Conference Proceedings, Parts 1 and 2, and/or to the Principal Author.

ACKNOWLEDGEMENTS

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The Committee would also like to thank the Policy and Planning Branch for sponsoring this year's conference.

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ABSTRACT

Recent Trends in Drinking Water Treatment

Vernon L. Snoeyink, Professor
of Environmental Engineering
University of Illinois
208 N. Romine
Urbana, Illinois 61801

Biological stabilization
of water
recent issue?
J. Wat. W. Association
Oct 84

Ontario Ministry of the Environment
Fifth Technology Transfer Conference
November 27 & 28, 1984
Holiday Inn-Toronto Airport
Toronto, Canada

The reaction to the finding that chlorination under certain conditions resulted in excessive trihalomethane concentrations has been a significant modification of chlorination practice. Chlorine dose has been reduced, breakpoint chlorination has been eliminated by some utilities, and many utilities now use combined chlorine instead of free chlorine. These changes will cause a greater frequency of problems caused by excessive microbial growth in distribution systems, such as taste and odor development, red water problems, and possibly regrowth of bacteria that are measured by the coliform test. Such problems will lead to a greater emphasis on water treatment to produce a biologically stable water before it is distributed. Many European utilities use biological water treatment processes such as fluidized-bed and packed-bed fixed film reactors to produce a water which can be distributed with low concentrations of residual disinfectant.

monochloramine
TOX = total organic halogens

Mitheim
break pt chlorination

NH_4^+ → promote growth of
micro-org.
 Fe^{++} Mn^{++}

DIRECT AND FOOD CHAIN UPTAKE OF ENVIRONMENTAL LEAD,
CADMIUM AND MERCURY IN A MODEL AQUATIC SYSTEM

note (change in title occurred)

Pamela Stokes, Institute for Environmental Studies and
Department of Botany, University of Toronto
and Peter Campbell, Institut National de la
Recherche Scientifique, University of Quebec

ABSTRACT

Recognising the theoretical and demonstrated relationships between metal speciation and biological uptake on the one hand, and pH of water on the other, we have reviewed the influence of pH on metal speciation in water and the influence of pH on metal-surface interactions at the cell/medium interface for a number of potentially toxic metals. Of these, sensitivity of speciation to changes in pH should be low for Ag, Cd, Co, Mn, Ni and Zn, moderate for Pb and high for Al, Cu and Hg; consideration of metal dissolution or desorption from solid surfaces was not included in the calculations. Supporting experimental evidence exists for Cu, Pb, Ag, Cd, Mn and Zn. In terms of biological uptake, not only the chemical speciation in solution but the effect of pH on the cell surface has to be taken into account. From the limited amount of experimental data in the literature, it can be shown that Cd, Cu and Zn are taken up (or exert toxic effects) more at neutral pH than at acidic pH. The simplest hypothesis to explain this is that competition occurs at the cell surface between the hydrogen ion and the metal ion. For Pb, low pH enhances uptake and toxicity.

Experiments on model food chains with defined media in which the speciation can be calculated tend to support this hypothesis for the first trophic levels (algae). It is proposed that the observed relationship for Hg, Cd and Pb in biota and pH in the field need to be considered mechanistically in terms of hydrogen ion effects on metal speciation, metal solubility, the cell surface, and (for all except algae) the indirect pathway through the food chain.

lakes subject to acidification. not heavily polluted.
mercury = algae + zooplankton compete with levels - first
high bio. factor of mercury.
not much dissolved lead - low does it get to fish + algae?
organic lead. rather of absorption.
very low levels of Cd - biota relate pH related levels.
Cd does not change its solubility due to pH change
found in acid lakes

ABSTRACT

STUDIES OF THE NITRATE DISTRIBUTION AND NITROGEN TRANSFORMATIONS
IN A SHALLOW SANDY AQUIFER NEAR ALLISTON, ONTARIO

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A recent survey showed a high proportion of domestic groundwater supplies in the unconfined sand-plain aquifer near Alliston to contain nitrate concentrations in excess of the drinking water limit of 10 mg/L NO_3^- -N. This study was undertaken to provide a more complete description of the spatial distribution of nitrate in the aquifer, to examine the factors responsible for the highly variable concentration distribution and to develop methods of groundwater development that would result in domestic supplies of improved quality.

Monitoring devices installed at several locations in the watershed showed the nitrate concentration versus depth to be highly variable. Under shallow water-table conditions, nitrate contamination was generally limited to depths of two to four meters below the water table. The decline in the nitrate concentration was generally matched by a decline in the dissolved oxygen concentration. These trends were similar to those observed elsewhere, and suggest that the depth of penetration of the contaminated zone is limited by the denitrification process. In areas with deep water tables, nitrate and significant concentrations of dissolved oxygen occurred across the entire saturated thickness of the aquifer. Laboratory tests conducted on core samples of the aquifer material suggested that under shallow water table conditions, sufficient labile organic carbon was transported to the water table to cause a substantial reduction in the dissolved oxygen concentration. With the development of reducing conditions, nitrate was converted to nitrogen gas by denitrification. Under deep water-table conditions, the data suggests that there was insufficient labile organic carbon reaching the water table to result in the development of reducing conditions and thus denitrification would not be a significant process in these environments.

Field tests indicated that in situations with stratified nitrate contamination, a substantial improvement in the quality of domestic supplies could be achieved simply by installing the intake zone of the wells at greater depth in the aquifer.

specific distribution
eg, trillium
borzoi acid

> sudden increase
at depth

ORGANIC CONTAMINANTS IN GROUNDWATERS AT SEVERAL ONTARIO LANDFILLS

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ABSTRACT

The occurrence and migration of contaminants in groundwater impacted by leachate at six municipal landfill sites are being studied to determine the hydrogeological, geochemical, and microbiological influences on their mobility and persistence. Of special interest are processes of attenuation (sorption, biodegradation) and dilution (hydrodynamic dispersion). Currently, studies are underway in sandy aquifers (CFB Borden, North Bay and Woolwich), less permeable sandy silty glacial till (CFB Borden), and in fractured shale and dolomite (Burlington and Hamilton). Studies at a landfill site on fractured clay-till in southwestern Ontario will begin in 1985.

At the North Bay site, where landfilling began in 1962, organic contaminants are found throughout the 1 km sandy aquifer. Chlorinated solvents are restricted to the immediate vicinity of the landfill, probably because of anaerobic biodegradation. Aromatic hydrocarbons may also be degraded in the final 300 m section. At the Woolwich site, the chlorinated solvents are migrating further while aromatic hydrocarbons are only found in low concentration even near the landfill. Aerobic conditions appear to dominate here, resulting in persistence of chlorinated methanes and ethanes and degradation of aromatics. Additional research into the hydrogeological controls of contaminant migration at these sites is underway.

At the landfill on sandy silty glacial till at Canadian Forces Base Borden, where landfilling began in 1976, a plume of groundwater contamination has developed that is readily mappable over a distance of 150 m based on chloride and total dissolved organic carbon. Detailed studies of the organic compounds in this plume will soon be initiated.

Contamination of a fractured bedrock system at the Hamilton site by organics has been difficult to define because the major contaminants are aliphatic and aromatic hydrocarbons which also occur naturally in these sedimentary bedrock strata. Therefore, research into the occurrence of hydrocarbons and S-bearing heterocyclic hydrocarbons in uncontaminated groundwaters is underway in order to identify better "leachate indicator" parameters.

At a landfill on fractured shale in Burlington, normal inorganic indicators of leachate contamination did not provide a basis for delineating the zone of contamination. At this site 1,1,1 trichloroethane, chlorobenzene and paradichlorobenzene at very low concentrations have been used to trace the zone of landfill impact for a considerable distance from the landfill.

Organic acids
Trichloroethane
1,1,1
chlorobenzene
paradichlorobenzene
10-100 ppb

EPIDEMIOLOGICAL STUDY OF DISEASE INCIDENCE AND RECREATIONAL WATER
QUALITY AT SELECTED BEACHES IN SOUTHERN ONTARIO
Nancy E. Brown and Patricia L. Seyfried, Departments of Community Health
and Microbiology, Faculty of Medicine, University of Toronto

Abstract

During the summer of 1983, a prospective epidemiological survey was conducted on weekends at six Southern Ontario beaches northwest of Toronto. The study area included: Claireville Conservation Area, Boyd Conservation Area, and Albion Hills Conservation Area, on the Humber River; Kelso Conservation Area, on Sixteen Mile Creek; Heart Lake; and Professor's Lake. A total of 9,296 persons were interviewed at the beaches and water samples were collected for microbiological analyses (total staphylococci, fecal coliforms, Escherichia coli, enterococci, fecal streptococci, heterotrophs, Pseudomonas aeruginosa, Campylobacter jejuni, Legionella sp., and viruses). Crude morbidity data revealed that persons who entered the water (7914/9,296 i.e.: 85%) experienced more overall illness ($p < .0001$ by Fischer's exact two-tailed test), respiratory ($p < .0001$), gastrointestinal ($p < .0001$), ear ($p = .0010$), eye ($p = .0024$), and skin ($p = .0202$) problems, than those who did not enter the water. Allergenic problems were not significantly different in the two groups ($p = .2640$). Microbiological analyses, collected both when the beaches were open (when epidemiological surveying was done) and when they were closed by officials, due to pollution problems, indicated that the geometric means per 100 ml. of water were: 432 for fecal coliforms and 370 for E. coli overall; 423 and 361 when the beaches were open; and 453 and 390 when the beaches were closed. The current guideline for fecal coliforms in the province of Ontario of 100/100 ml. of water was exceeded. Investigation is currently underway to correlate the epidemiological and microbiological data, and to evaluate the value of the existing guideline.

VOLATILIZATION RATES OF ORGANIC CHEMICALS
OF PUBLIC HEALTH CONCERN

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Toronto, Ontario

ABSTRACT

A study of volatilization of organic chemical compounds of public health concern from streams and rivers has been carried out. The volatilization rates are expressed in terms of liquid film coefficients (K_L). The K_L values of ethylene gas are determined from data on ethylene and rhodamine WT dye concentration distributions which were collected in provincial streams and rivers of differing hydraulic characteristics.

Relationships among K_L , channel hydraulic parameters and chemical properties of organic compounds have been developed through statistical analyses as well as dimensional analysis using the Buckingham π -Theorem. The relationships for ethylene gas, derived from the dimensional analysis procedure, have been found to provide better correlations with the observed K_L values. A sensitivity analysis of various parameters on K_L has also been carried out. A statistical relationship developed by Rathbun and Tai (1982) has been found to underestimate K_L values for the provincial streams and rivers. An evaluation of the theoretical relationships between K_L and molecular properties (critical volumes and molecular weights) using experimental data reported in the literature has revealed that the relation between K_L and critical volume is suitable to calculate K_L values for highly volatile organic chemicals using the known K_L values of ethylene gas or other compounds (eg. propane, benzene); however, for moderate and low volatile compounds, no relationships could be obtained from the available data.

The computation of K_L for a given organic compound using the relationships developed in this study is outlined in a step-by-step procedure. An example illustrates the various computations involved. In general, the method is applicable to volatile compounds with Henry's law constants greater than 10^{-3} atm-m³/mol.

EXPERIMENTAL AND ENVIRONMENTAL MODELLING STUDIES OF
HAZARDOUS/CHEMICALS

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and Applied Chemistry, University of Toronto

ABSTRACT

Progress is described on an environmental modelling project which, it is hoped, will be used to assess the behavior of chemicals in Ontario. A Level III fugacity model has been compiled which can be used to calculate the behavior of a chemical which is subject to steady state partitioning, reaction, advection and intercompartmental transfer in an evaluative environment consisting of six compartments, air, soil, water, bottom and suspended sediments and fish. The model is applied to 14 chemicals of varying properties and is shown to generate behavior profiles which are consistent with reported chemical fate observations in the real environment. Since this single model generates a set of consistent behavior profiles, it is suggested that it may be useful for predicting the behavior of chemicals for which no environmental observations yet exist. Environmental processes which are still inadequately treated by the model are discussed with a view to later improving the model's predictive reliability.

In a parallel effort (published in July 1984) we have addressed the issue of characterizing the heterogeneous spatial distribution of a chemical using probability density functions.

A Southern Ontario model is being developed which attempts to combine the principal features of the evaluative model with the spatial distribution approach and can be used to assess the environmental fate of chemicals in that region.

Technology Transfer Conference No. 5,
Holiday Inn, November 27 & 28, 1984

CHEMICAL IDENTIFICATION AND BIOLOGICAL ASSAY OF
ENVIRONMENTAL MUTAGENS, PROMOTERS AND INHIBITORS

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Abstract

Chemical Identification and Analysis of Polynuclear Aromatic Hydrocarbons (PAH):- Earlier studies of the extraction and recovery of PAH in water samples by adsorption on C₁₈ Sep-Pak cartridges and analysis by HPLC indicated that quantitative recovery was dependent upon pH of the sample (Technology Transfer Conference No.4). Consequently, the effect of variation in pH of the water samples on the efficiency of recovery of 16 PAH compounds, listed as high priority pollutants, was determined over the range of pH 7, 5, 4, 3 and 2. The lower molecular weight PAHs, consisting of 2 and 3 aromatic rings, can be recovered in high yield at pH 7. Fluoranthene and pyrene can also be recovered in yields of over 90 percent at pH 7. However, more complex PAHs of higher molecular weight require adjustment of the water samples to pH 3 or 2 for optimum recovery. The influences of flow rate of water sample and concentration limits of PAH on quantitative recovery by trace enrichment through Sep-Pak cartridges were also investigated.

Biological Assay of Environmental Mutagens, Promoters and Inhibitors:- The effects of four potential inhibitors, such as α -naphthoflavone, ascorbic acid, caffeic acid and ethoxyquin on pairwise combinations of promutagens and direct-acting mutagens were determined by means of the Ames Salmonella typhimurium test. The bone marrow micronucleus assay on mice was employed to determine the inhibitory activity of fumaric acid, thioacetamide, glutathione and β -carotene on promutagens and direct-acting mutagens in mice.

The effects of pairwise combinations of promutagens and direct-acting mutagens in mice were studied by means of the bone marrow micronucleus and abnormal spermhead assays. 7,12-Dimethylbenzanthracene (DMBA) and benzo(a)pyrene (BaP), in combination, yielded a non-additive or antagonistic response. Whereas additive responses were found with DMBA plus cyclophosphamide (CP); BaP and CP; BaP and mitomycin C (MMC); CP and MMC. In the sperm abnormality assay, pairwise combinations of DMBA plus CP; and BaP+CP showed additive responses. However, non-additive responses were produced by combinations of DMBA+BaP; DMBA+MMC; CP+MMC; and BaP+MMC.

Collaborative Study on Short-Term Tests For
Genotoxicity and Carcinogenicity

D.M. LOGAN

Department of Biology, York University

ABSTRACT

For the last two years we have participated in an international genotoxicity and carcinogenicity study established by The WHO, UN and International Labour Office. The aim of this study is to develop a battery of short term tests by which chemicals may be assessed quickly and at relatively low cost for potential genotoxic hazard. The chemicals which we have used (Benz (a) pyrene, pyrene, 2-acetylamino Fluorene and 4-acetylamino Fluorene) are ones for which extensive whole life data is available for comparison. The assays tested were two in vivo assays, the bone marrow micronucleus test and the abnormal spermhead test. In addition we have tested the effect of two different routes of administration on the sensitivity and response of the two assays, i.e. Intraperitoneal injection and gavage: Benz (a) pyrene, a known carcinogen gives a positive reaction in both assays while pyrene does not. 2AAF another known carcinogen also gives a positive reaction in both assays while the isomeric 4AAF does not. These data should be contrasted with bacterial tests in which the noncarcinogens nevertheless produce mutations and hence are scored as carcinogen positive. These assays, particularly in common, therefore appears to offer a higher degree of selectivity than that available in bacterial assays.

Seven additional chemicals including the two pesticides Mirex and Atrocine which are of particular interest to the Ontario Ministry of The Environment were also tested and these data will also be presented.

THE DEVELOPMENT OF A FRESHWATER FISH TEST
TO IDENTIFY AQUATIC TOXIC CONTAMINANTS

I.R. Smith and V.E. Valli, 1984

Department of Pathology,
Ontario Veterinary College,
University of Guelph,
Guelph, Ontario, N1G 2W1.

ABSTRACT

Approaches to assess mutagenicity and/or carcinogenicity in all fish species are necessary to facilitate routine monitoring and trend analysis of genotoxic inputs. The suitability of fish embryos and juveniles, and of techniques for detecting chromosome damage, were determined utilizing Brachydanio rerio (Zebrafish) as a model species. Previously published results (Smith and Valli, 1983) were encouraging, and further investigations are reported here.

The acute effects of Ethyl methanesulphonate (EMS) included teratogenesis after both 24 hour and 8 day embryo exposures, which could be related to tissue (cell) death. In addition, latent effects evident after short-term exposure periods included mortality and inherited mutations in epidermal cells (leading to cell death through apoptosis). A latent effect not induced by EMS (after 6 months observation) indicates that the genotoxicity observed in embryos did not lead to neoplasia.

Further genotoxicity analysis revealed that newly fertilized embryos were more sensitive than 6 hour old embryos, and that erythrocytic micronuclei (30 hours of age) were a more sensitive endpoint than yolk-sac micronuclei. The most sensitive measure of genotoxicity yet examined (24 hour anaphase aberration analysis) indicates a sensitivity equivalent to published results utilizing adult fish and more complex techniques.

The sensitivity and wide applicability of fish embryos (plus the relatively low cost) make the examination of either laboratory or feral fish, exposed in the laboratory or in situ, a promising technique. The examination of temporal and spatial variability of genotoxicity endpoints in wild fish embryos as they relate to industrial discharges may be the most promising application. Further applications include assessing the relative impacts of parental chemical contributions, or water uptake, and the further study of latent effects, including neoplasia and mutations.

FIELD MEASUREMENT OF INFILTRATION THROUGH LANDFILL COVERS

BY

A.G. Hims, - Gartner Lee Associates Limited
P.K. Lee - Gartner Lee Associates Limited
R.W. Gilham - University of Waterloo,
Earth Science Department

ABSTRACT:

This paper reports the final results of the Phase 1 Study which was to design, construct and field test instrumentation capable of measuring the infiltration which occurs through the final cover material at a landfill site. The study was initiated in 1982 and collection of data has been on-going since March 1983. Details of the lysimeter design and construction, together with the initial results, were reported in the proceedings of the Fourth Annual Technology Transfer Conference in November 1983. An analysis of all data obtained between March 1983 and July 1984 is now presented, with an assessment of the overall outcome of this phase of the study.

ABSTRACT

Development of Specific Protein Adsorbents for Selective Extraction of Trace Contaminants Significant to Human Fetal Health: Modelling of Fetal Cross-Placental Uptake Specificity

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The complementary ligand binding specificities of maternal serum albumin and fetal alpha-fetoprotein (AFP) for nutrients e.g. polyunsaturated fatty acids (PUFA), and metabolic wastes e.g. bilirubin, have been proposed to provide a specific mechanism for the transport of these ligands across the mammalian placenta. We have developed an in vitro assay to demonstrate the principle of this mechanism. This assay shows that in the presence of AFP and albumin, PUFA as well as a known cross-placental teratogen, diethylstilbestrol (DES), bind specifically to AFP. Using radiolabelled fatty acids and DES, we have shown that 1 umole of AFP in a ConA-Sepharose column retains greater than 95% of PUFA and 90% of DES when nanomolar solutions of these ligands pass through the column. We propose that AFP is responsible for the uptake and concentration of both PUFA and DES in the fetal circulation. On the assumption that other biohazardous substances which have high AFP-binding affinity are likely to be similarly concentrated in the fetus, we believe that the binding specificity of AFP can be used for the extraction of trace environmental contaminants significant to human fetal health.

ABSTRACT

EFFECTS OF EXPOSURE TO LEAD, CADMIUM AND MERCURY ON THE TISSUE OF YOUNG FISH AND RATS

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and

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The response of the kidney and liver, both in mammals and fish exposed to cadmium and mercury involves the stimulation of transcription of the genes to provide messenger RNA (mRNA) for metallothionein species. However recent work shows that neither tissue metal levels nor tissue metallothionein levels indicate functional impairment or functional reserves in the tissue. The situation is even more complicated with Pb^{2+} exposure since there is no triggering of metallothionein gene transcription. However we have found that (1) the livers of rats do have increased messenger RNA for certain proteins which are released into the blood and (2) the kidneys of rats do have increased mRNA for a prominent protein-splitting enzyme, urokinase.

In addition to these different genetic responses to Cd^{2+} , Hg^{2+} and Pb^{2+} , the enzyme function at the kidney membrane/urine interface (i.e. the brush border membrane) has been studied in rats. Either an acute dose of Pb^{2+} (10 mg Pb^{2+} /kg body weight) or chronic administration of Pb^{2+} in acidified drinking water (500 mg/l) for 3 or 6 weeks exert effects on the brush border membranes which are not correlated well with the Pb^{2+} level in the fraction and which are not accompanied by detectable changes in the membrane or in the urinary function. The same was true after an acute dose of Cd^{2+} . The effects on enzyme activity result from some mechanism not related to a direct effect of the heavy metal and the effects would be undetected if the animals were not sacrificed for the analysis.

Thus we have analyzed the muscle of Pb^{2+} exposed animals to see if a more accessible tissue could provide evidence for heavy metal exposure. The mRNA obtained from the muscles of rats given Pb^{2+} alone, Cd^{2+} alone, or Pb^{2+} plus Cd^{2+} , all showed increased activity, greatest in the Pb^{2+} + Cd^{2+} experiment, especially for a protein believed to be glyceraldehyde-3-phosphate dehydrogenase. This is an enzyme affected by heavy metals in vitro, and thus the gene transcription product, mRNA, may be produced in increased amounts as a compensatory response.

In studying the muscle of a different animal, namely fish, exposed to acidified water containing 100 μg Pb^{2+} /l or 500 μg Pb^{2+} /l this enzyme exhibited decreased activity. The liver and gonads of the fish also exhibited changed activities for certain enzymes. A much lower Pb^{2+} level in the water (5 μg Pb^{2+} /l) has been used for much longer periods (5 months rather than 3-6 weeks) in order to see what minimal levels of Pb^{2+} could be tolerated with no development of changes in these very sensitive parameters of tissue function.

**REMOVAL OF HAZARDOUS CONTAMINANTS IN THE
HAMILTON WATER POLLUTION CONTROL PLANT**

by

G. Zukovs, R.J. Rush, M. Gamble

CANVIRO CONSULTANTS LTD.

Abstract

An assessment is presented of the incidence and removability of selected hazardous organic and inorganic contaminants (HCs) at the Hamilton WPCP. The principal study objectives were to evaluate the annual HC loadings entering and being discharged from the WPCP and to determine the present process efficiency for and factors influencing HC removal. HC monitoring included the solid and liquid phase concentrations of total PCBs and other selected chlorinated organics, PAHs and heavy metals. As well, extensive monitoring of conventional parameters was conducted in order to characterize both unit process (e.g. primary treatment) and overall plant performance.

Results indicate a high degree of overall removal (>97% for WPCP as a whole) for the PAHs. Total PCBs were similarly well removed, averaging 90%. Both lindane and pentachlorophenol were removed to a lesser extent (70% to 63%) and with considerably less consistency. Heavy metals removals were generally in excess of 80%.

Results further indicated that as an overall average of all the HCs monitored, approximately 20% of the loadings originated from the in-plant return stream. This varied considerably between specific contaminants being less than 10% for some PAHs, 52% for pyrene, 12% for nickel and 20-25% for the other metals.

ABSTRACT

Assessing the Behavior of Hazardous Liquids
Spilled Onto Soils

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Department of Civil Engineering
University of Waterloo

This paper describes the current status of research assessing the behavior of immiscible hazardous contaminants in soil. The work is supported in part by Provincial Lottery Funds and is being performed in the Department of Civil Engineering at the University of Waterloo.

A major portion of the research involves the simulation of immiscible liquid behavior in soil through the use of computer models. This includes (i) a model for spills onto soil with overland flow, penetration and evaporation, (ii) a model for the transport of immiscible liquids in soil either saturated or unsaturated, and (iii) a model for the movement of hazardous vapours in unsaturated soil.

Another area of research is experimental in nature but is only in its initial stages. It involves (i) the development of methods to detect immiscible liquids in soil through measurements of dielectric coefficients, thermal conductivity and electrical conductivity, and (ii) the performance of experiments to yield information on the flow of immiscible liquids in soil, especially the relationships between relative permeability, capillary pressure and percent saturation.

Research is also in progress to develop a spill response model which incorporates the behavior of the spilled liquid including overland flow, penetration, evaporation and transport within the soil and also recommends remedial action specific for the incident.

A literature review on the subject is near completion. It has approximately five-hundred references and was prepared with the assistance of a key-word information storage and retrieval system developed on a microprocessor for this research.

EFFECTS OF METALS FROM MINE TAILINGS ON THE MICROFLORA OF
A MARSH TREATMENT SYSTEM

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Faculty of Medicine, University of Toronto

ABSTRACT

The artificial marsh system is an ideal solution for wastewater treatment in smaller communities. Several artificial marsh systems have been constructed in Ontario, including Cobalt and Listowel. These two systems possess similar construction patterns except for the fact that Cobalt's marsh system is built on a mine tailings basin. Consequently it is necessary to determine if the metals that may elute from the tailings can exert a serious toxic effect on the microbial activity required for proper waste treatment.

In this study, the toxic effect of eleven different metals, as well as metal mixtures, on bacterial isolates from the Cobalt and Listowel marshes were determined. The agar plate test, the resazurin reduction procedure, and the ATP luciferin luciferase reaction were used for toxicity testing. Of the three methods, resazurin reduction was found to be the least effective in assessing bacterial resistance to heavy metals.

As might be expected, bacteria recovered from the Cobalt marsh were more metal resistant than isolates from the Listowel marsh treatment system. It is important to note that strains of eight genera isolated from the marshes were susceptible to lower concentrations of metals when metal mixtures were tested.

Sampling sites in the marsh systems were monitored for heterotrophic bacteria, total coliforms, fecal coliforms, Escherichia coli, fecal streptococci, and Pseudomonas aeruginosa. Results showed that both the Cobalt and the Listowel artificial marsh treatment systems were responsible for substantial reductions in levels of these bacterial parameters. By comparison, the natural marsh system at Cobalt was much less efficient at reducing bacterial numbers from the inflow to the outflow sites.

REVISED MONITORING SCHEME FOR PERSISTENT AND TOXIC ORGANICS
IN GREAT LAKES SPORTS FISH

J. A. Coburn and H. Huneault, Zenon Environmental Inc. and
G. Rees and G. Crawford, Ontario Ministry of the Environment

ABSTRACT

Protocols for the analysis of a broad range of synthetic organic compounds have been identified and evaluated on fortified and unfortified fish tissue samples. Recoveries of the trace organics have been determined at low parts per million and parts per billion concentrations. Sample extracts were processed using gel permeation chromatography (GPC) for elimination of lipids from the trace organic fraction prior to full scan gas chromatographic-mass spectrometric (GC/MS) analysis. Data will be presented on the sample preparation protocol and the GC/MS analyses of fish samples from the Great Lakes. These latter data will include contaminant identifications as well as spatial trends for selected chemicals in several fish species.

HEAVY METAL MOBILIZATION AND BIOLOGICAL UPTAKE:

COBALT MINE TAILINGS

by

E. Hanna
JE Hanna Associates Inc.

Abstract

The objective of the study was twofold. The first was to assess the potential and significance of heavy metal leaching and uptake from mine tailings in Cobalt, Ontario and similar biophysical environments. The second was to explore the impact that construction (on the tailings) of an artificial marsh designed to treat municipal sewage might have on heavy metal cycling.

The primary element of the study was a series of simulated leaching experiments using cores of tailings to observe the effects of i) ionic strength of the leaching solution, ii) water table elevation and iii) redox levels on metal mobilization. The results of the experiments were corroborated with field data. Biological uptake and cycling was assessed using cultures of duckweed (Lemna minor).

The results of the work demonstrated that a large range in the mobilization rate of heavy metals occurred over the treatments used for the experiments. In addition, most metals were in highly available forms.

ABSTRACT

WATER QUALITY CHARACTERISTICS OF TROUT FARM EFFLUENT

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The water quality characteristics of eight private trout farms in Ontario were investigated over a four month period from June to October 1983. Each farm was visited three times during this period and parameters such as water flow rate, trout farm biomass, feed and feeding system and water chemical parameters such as ammonia (NH₃), and phosphorus (P, total phosphorus) were measured and collected. The results indicated that the major water quality parameters affected by the trout farms were NH₃ and P. The daily loading of P from the trout farms ranged from 59 to 1299 g/day which was highly correlated to the biomass of the individual trout farm. In addition, the NH₃ loading from the trout farms ranged from 1.8 to 14.1 kg/day. However, in contrast to the P loading, the NH₃ loading did not appear to be highly correlated to the trout farm biomass which was unusual considering that ammonia is supposed to be the major nitrogenous waste (>90%) of fish such as rainbow trout. There appeared to be some beneficial effect of having either a settling or a retention pond at the trout farm in order to reduce the loading of NH₃ or P. However, this conclusion requires further study and verification due to lack of standardization of the various trout farms. In addition to the trout farm effluent study, a number of diet-growth studies were conducted to determine the effect of diet on phosphorus retention in rainbow trout. These studies indicated that supplementation of commercial trout diets, containing 25% fish meal in the feed formulation, with dicalcium phosphate was unnecessary. Furthermore, the formulation and feeding of high protein-energy diets to rainbow trout significantly increased phosphorus retention in these fish. On the basis of these results, it would appear to be possible to reduce phosphorus excretion in the trout by dietary manipulation. The formulation and processing of low-pollution trout diets could be of benefit to trout farms where NH₃ and P loading exceeds governmental regulations. (Supported by OMAF and OME)

DESIGN OF GROUNDWATER MONITORING PROGRAMS
FOR WASTE LANDFILL SITES

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ABSTRACT

The increased concern over groundwater quality monitoring at waste landfills has resulted in many advances being made in sampling techniques, contaminant transport modelling and legislation for groundwater protection. However, little work has been done to systematically design monitoring programs by incorporating into design procedures sampling costs, data variability, environmental damage costs and probabilities of contamination.

The research to be reported here demonstrates how a hierarchy of models of increasing complexity for monitoring program design can be built up from basic hydrogeological, statistical, economic and optimization concepts. The monitoring program design is for detection-type monitoring concerned with observing significant changes in water quality, and where remedial action is initiated upon detection. The tradeoff between periodic monitoring cost and the increased remedial action costs resulting from undetected plume growth is expressed mathematically. The effect on the total cost of monitoring and remedial action by decision variables, such as the number of monitoring wells, the frequency of monitoring and the significance level of the statistical test used for impact assessment, is investigated.

ABSTRACT

The Utility of Microsomal Monooxygenase Activity Assays in Health Risk Assessment of Exposure to Airborne Emissions of Chlorinated Dibenzodioxins and Dibenzofurans

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Halogenated dibenzodioxins and dibenzofurans have been quantified in stack gas emissions from a variety of stationary combustion sources. Quantitations have been reported in ng/m^3 and $\mu\text{g/m}^3$ levels. The most comprehensive data basis usually include tri through octachlorinated homologous groups instead of individual congeners. Speciating individual compounds is made difficult because of a world-wide deficiency in analytical standards. Thus, regulators are left with evaluating the health ramifications of human exposure based on a mixture of compounds as whole groups of compounds. A dilemma arises with regard to risk assessment because not every CDD or CDF isomer within each homologue is equal in toxicity, teratogenicity, or carcinogenicity, and the 2,3,7,8-TCDD congener remains the most extensively evaluated compound. Within the past decade significant advances have been made in observing the action of aryl hydrocarbons on a macromolecular level. A mechanism of eliciting the toxic response is postulated to occur by the CDD or CDF compound binding to a cytosolic receptor protein, then translocating to the cell nucleus and producing a coordinate induction of a number of enzymes including AHH and other microsomal monooxygenase activity. Receptor assays and AHH assays using various CDD/CDF congeners have shown a good correlation with enzyme induction and the pleotypical toxic response in rats and mice. Can this macromolecular mechanism be used in risk assessment to evaluate exposure to homologous groups of compounds? The utility of the microsomal monooxygenase activity assays in risk assessment will be discussed.

EVALUATION OF CONTAMINATED WATER AND SOIL SITES
AS SOURCES OF AIRBORNE HAZARDOUS MATERIALS

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ABSTRACT

Progress is reported on a project to develop two test procedures for estimating experimentally the emission rates into the atmosphere of chemical contaminants from soils and water. The work has involved the development of test equipment and specifications for operating conditions, the selection of "benchmark" chemicals and standard soils and water media. Two brief computer programs are being written to simulate the results from the test system and translate these results to the real environment.

THE CHEMORECEPTIVE MEMBRANE AS AN ELECTROCHEMICAL SENSOR FOR TRACE ORGANIC SPECIES
IN THE ATMOSPHERE. M. Thompson, U. J. Krull, A. Arya, E. King and H. E. Wong,
Department of Chemistry, University of Toronto

ABSTRACT

The thesis of the Chemical Sensors Group at the University of Toronto is that a selective chemical sensor configuration can be based on modulation of the transmembrane ion flux through thin lipid membranes by a stimulant (analyte)-chemoreceptor interaction at the membrane surface. In previous M. of E. Technology Transfer Conferences we have expounded theoretically and experimentally on this concept, and discussed examples of potential mechanisms for gas-sensing. In order to reach the ultimate goal of a discrete and integral sensor, it is clear that a robust system must be developed which involves supported thin film membranes on electronic devices such as chemically-sensitive transistors. In this regard, the Group has recently been examining the nature of molecular packing in lipid/cholesterol monolayers by analytical Langmuir-Blodgett experiments for correlation with Arrhenius-Eyring results on membrane ion conduction. Also, preliminary experiments have been performed on deposition of Langmuir films on hydrophilic substrates. The former work demonstrates clearly that internal membrane functions that are responsible for ion conduction can be controlled from the membrane surface. Secondly, some limited success has been achieved with respect to deposition of electrically functional films which respond to known electrochemical stimulants. Finally, the future possibilities with respect to device configurations, gas-sensitive chemistry, artificial intelligence and applications will be outlined.

Gas-phase Photochemistry of PCB's

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We have been studying the gas-phase photochemical degradation of chlorinated aromatic compounds in static systems. Both chlorinated benzenes and chlorinated biphenyls behave similarly. Product studies reveal that the principal photochemical reactions of these substances parallel those observed in solution, with the products explicable for the most part in terms of a simple C-Cl homolysis



A series of kinetic experiments showed that the disappearance of all the aryl chlorides studied follows a first order rate law. Procedures had to be developed to ensure that all of these rather involatile compounds were actually in the gas phase.

The present task at hand is to relate these rates of photodegradation to quantum yields. We have developed a simple procedure to allow this measurement to be made quickly, and hope to have some absolute quantum yields to present at the time of the conference.

ABSTRACT

THE HAMILTON STUDY: Refinement of SO₂ and Particulate Data for Exposure Estimation

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A study to investigate the effects of environmental factors on the respiratory health of 3500 children aged 7 to 10 years was conducted in Hamilton, Ontario from 1978 to 1982. Respiratory health was assessed by pulmonary function testing and by questionnaire, and environmental factors were determined from the questionnaire and by field measurement of air quality. Measurements were made of levels of sulphur dioxide (SO₂) and suspended particulate matter. Two groups worked together on the project: one group carried out the epidemiological survey and the measurement of total suspended particulate (TSP) and particle size distribution (PSD); the other group carried out the field measurements of SO₂ and the development of new instrumentation (laser absorption spectrometer-LAS) for more sensitive measurement of SO₂.

In order to estimate exposure of the children to ambient air pollution, we decided to input the data obtained at each site (for SO₂, TSP, and PSD) into a quadratic response surface model for each pollutant, based on monthly average values for each site. From the response surfaces in pollutant concentration, and in easting and northing geographical co-ordinates, we could estimate exposures specific to each of the 49 schools in the study, and thereby calculate for each child a yearly exposure based on the time he or she was tested at that school. By examining the response surfaces visually, we determined that there were serious discrepancies in the data, especially for measurements of SO₂; thus, we found it necessary to implement a data recovery programme which included rereading the original SO₂ recorder charts. This experience has demonstrated the need for explicit manuals for the documentation and quality control of air pollution data, a process which we had already implemented for the particulate data. Relatively few problems have emerged in deriving particulate exposures.

(Supported by Ontario: Environment, and Health)
(Canada: National Health and Welfare)

ABSTRACT

The Dispersal of Airbourne Particulates on a Short- and Long-term Scale

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The local meteorological conditions, especially the wind velocity, are important when assessing the dispersal of air particulates from localized sources such as foundries and traffic intersections. To provide this information when measuring the element concentrations on an hourly basis with a streak filter, a microprocess-controlled meteorological station measuring components of the wind velocity, rain fall, temperature and light intensity has been constructed.

The system samples the parameters every seven seconds and stores a thirty-minute average of each parameter for later correlation with the element concentrations in the deposits. Besides monitoring the weather conditions, the microprocessor also records a thirty-minute average of the air flow through the sampler. The latter is found to vary significantly, possibly due to the relative humidity, and therefore needs to be known if accurate concentrations are to be determined. It is planned to install a transducer to measure this parameter.

The project to determine annual variations in pollution through the observation of element variations in tree rings has continued. Cores from several more trees from Sudbury have been examined with emphasis placed on measuring the lighter elements Si, Al and Mg. When PIXE analysis is done in air, the air path from the target to the Si(Li) detector strongly attenuates the X-rays from these elements. To reduce this problem, the detectors have been fitted with teflon cones extending to within a few millimetres of the target and hydrogen gas is bled into these cones to displace the air. Attenuation of the X-ray intensity is then only due to the detector's Be window. Interest in these elements arises from the conjecture that acid rain lowers the pH of the soil so that elements such as Al are freed from their minerals. These experiments are designed to test whether the concentrations of such elements increase in the rings with higher levels of acid rain.

ABSTRACT

MONITORING GENOTOXICITY IN THE ENVIRONMENT USING SISTER CHROMATID EXCHANGES IN MICE.

M.L. Petras and R. Piscitelli, Department of Biology, University of Windsor, Windsor, Ontario.

Studies involving the exposure of tissue culture cells and of laboratory animals (via injection) to genotoxic agents have shown sister chromatid exchange (SCE) analysis to be a sensitive test for the detection of mutagenic and carcinogenic agents. Recently we suggested using the SCE test to monitor general genotoxicity levels in the environment by determining SCE levels of mice living in that environment. This report describes the procedure that has been developed, the results of the application of this procedure to mice inhabiting natural habitats and some of the limitations of this approach.

The SCE detection procedure which proved most suitable included the implanting of paraffin coated 5-bromo-2'-deoxyuridine tablets subcutaneously and staining slides with Fisher's Giemsa after they had been immersed in Hoechst 33258 and exposed to strong fluorescent lights for approximately 24 hours. These changes in the standard procedure allowed the routine processing of 20 samples per day. The limiting aspect is now the typing of slides since one person can routinely score no more than 6 per day.

C3H mice were used to standardize the procedure and as controls in all of the runs. C3H mice (61) gave a mean SCE value of 4.30 ± 0.516 . Also 20 DBA/2J mice tested gave an overall SCE value of 5.23 ± 0.75 . In either group there were no major deviations from the mean of the group.

Wild mice (285) from corn cribs gave a mean SCE value of 5.72 ± 1.08 . There were, however, both geographic and temporal fluctuations. Mice collected in early spring, prior to crop spraying, gave SCE values of 5.93 ± 1.07 (17 mice) and 4.83 ± 1.25 (19 mice) from the Windsor and Ridgetown (96 km east of Windsor) areas, respectively. These results are consistent with those reported earlier. Temporal variations were most pronounced in the Ridgetown populations where the early May (prespraying) SCE values were 4.83 ± 1.25 (19 mice), the mid-May (spraying period) SCE counts were 6.77 ± 1.12 (16 mice), the mid-June (early post-spraying) values were 4.58 ± 1.20 (15 mice) and the late July values were $4.15 \pm .79$ (14 mice). The Windsor samples gave similar results.

To complement the work on wild mice, both C3H and DBA mice (90) were housed in twenty-gallon enclosures partially filled with corn. The results are consistent with those observed in wild mice.

Several experiments were also carried out in an attempt to elevate SCE values drastically. C3H mice were exposed to the herbicide bentazon (Basagran) for one hour and 8 hours while a field was being sprayed. Bentazon, a postemergent herbicide used on corn, was the most common spray used in the study area. The mean SCE values were 4.93 ± 0.52 (8 mice) and 5.45 ± 0.24 (8 mice), respectively. These results indicate that even a brief exposure to this herbicide will effect SCE values. Mice were also placed in an industrial setting where high concentrations of organic solvents were used. A three day exposure resulted in an increase of SCE levels in all six mice examined (mean = 5.22 ± 1.08).

Overall our results indicate that the SCE test will detect increases in genotoxic levels. These increases, some of which are due to widespread agents and others to localized factors, elevate SCE levels by from 25 to 50%. At least at present, such increases must be considered minor. Areas where high levels of genotoxic agents exist have not been satisfactorily identified. Results of such situations are essential before a conclusion on the value of the SCE approach is reached.

(This work is supported by a grant from the Ministry of the Environment, Ontario.)

QUANTIFICATION OF ASBESTOS AIR POLLUTION IN ONTARIO

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ABSTRACT

Asbestos, a well known carcinogen, is estimated to account for almost half of all occupationally related cancers. The potential carcinogenic effect associated with even extremely low levels of asbestos is a major consideration in establishment of environmental asbestos standard for outdoor air.

In order to accurately assess the health risk associated with asbestos air pollution, the dose response curves based on optical microscopic (OM) fibre counts needs to be extrapolated downward in the size ranges of fibres only visible by Electron Microscopy (EM). Various factors that affects this relationship have to be considered. The presence of long thin fibres ($d < 1.5 \mu\text{m}$ and $L > 8 \mu\text{m}$) that are considered most carcinogenic, in outside air is another critical factor.

Data on analysis of Environmental samples as well as occupational samples will be presented.

Sweet Corn, Cabbage, Cauliflower and Rutabaga Responses
to Air Pollution in Southern Ontario

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Abstract

Replicated field experiments were conducted in 1984 at the University of Guelph - Ontario Ministry of Agriculture and Food Research Station at Cambridge, Ontario; at the Ontario Ministry of Agriculture and Food Horticultural Experiment Station at Simcoe; and at the Canada Department of Agriculture Research Station at Harrow. Randomized block split-plot experiments were conducted with control (water), benomyl and mancozeb chemical protectant sprays applied to the plants weekly throughout the growing season. The use of these chemical protectant sprays was based on laboratory studies with a wide range of chemicals and on literature references. There were six cultivars of corn and two each of the other three species at each location with one planting date for sweet corn and two planting dates for cabbage, cauliflower and rutabaga. Cabbage and cauliflower plants were set up with transplants while seeds were used for sweet corn and rutabaga. Tobacco indicator plants of the cultivar 'Bel W-3' were placed in each plot. The extent of leaf injury on the tobacco plants was evaluated weekly. Injury on the tobacco leaves correlated well with ozone monitoring data. Harvests of these plots are continuing. Yield data analyses and interpretation are not yet complete and will be reported later.

Abstract

The impact of ozone on potato and peanut in Ontario

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In an attempt to establish dose-response functions for O₃ impact on various crops a number of approaches have been used. The approach used most widely in the U.S. is open-top chamber method. This method is costly and therefore other approaches have been evaluated.

The antioxidant, EDU, which was very effective in reducing bronzing in white bean, has been used on potato and peanut for several years. Control of oxidant injury on potato with EDU is only partial, and does not appear to provide a very accurate estimate of yield losses in O₃-sensitive cultivars. EDU gave effective control of oxidant injury in peanut with significant yield responses in sensitive cultivars.

EDU treatments were used to estimate what yields would be without significant oxidant injury and to compare the yields to those of insensitive cultivars. Yield differences between sensitive and insensitive cultivars, attributable to O₃, were used to develop a dose-response function using cumulative O₃ dose for July and August.

Developing the dose-response function for potato presented some major difficulties because of large gaps in the O₃ data base for past years and for gaps in cultivar yield data at Simcoe for sensitive cultivars.

The yield data for peanut were more complete, but spanned fewer years. Using differences in yield between sensitive and insensitive cultivars in cultivar trials offers another approach to establishing dose-response functions, but is dependent on consistent monitoring data.

DIOXINS AND FURANS: ANALYTICAL METHODOLOGY, LEACHATES AND
CONDITIONS FOR CONDENSATION-DESORPTION ON STACK PARTICULATES

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ABSTRACT

It is now known that dioxins and furans enter the environment from combustion processes and commercial chemicals. Although there are established methods used for their analysis in water, sediment, biological tissue and particulate matter, methodology improvement and study is necessary to fill in gaps in our detection ability. Several of these related studies are currently being conducted. All these methods depend upon GC/MS techniques.

Methodology for the analysis of dioxins at ultra-trace levels (parts-per-quadrillion) employing AMBERLITE XAD-2 resin is presented. Apparatus for on-field sampling has been designed comprising of a magnetically coupled gear pump, stainless steel tubing, glass fiber filter, a stainless steel column containing the resin, and two flow meters. In the first phase of the project, the testing of the resin, adsorptive losses to glass and teflon precluded the complete characterization of the resin. The second phase of the project is currently underway where actual sampling of the influent and effluent from an Ontario water treatment plant will be sampled.

The absorption and desorption rates of dioxins and furans on flyash are being studied. Flyash from the Commissioner Street incinerator was heated in a pyrex tube under a flow of nitrogen. Organic material desorbed from the first sample was collected on exhaustively extracted flyash downstream. Three temperatures and three nitrogen total volumes were investigated. The desorption losses of dioxins were determined for the heated flyash sample using tetra-, penta-, hexa-, and hepta-chlorodibenzodioxins as external standards.

Procedures for the analysis of organic contaminants in water treatment chemicals are being developed. The water treatment chemicals examined are inorganic materials in the form of solids or aqueous solution. Solid samples are Soxhlet extracted and subsequently analyzed by gas chromatography/mass spectrometer (GC/MS). For liquid samples, the organics are extracted from the aqueous medium into an organic solvent using liquid-liquid extraction techniques. Compounds tentatively identified by GC/MS analysis include branched alkanes and alkenes, long chain alcohols and fatty acids, various substituted cyclic and aromatic compounds, phthalates and their derivatives, ketones, nitrogen-containing compounds, sulfur-containing compounds, and some halogenated hydrocarbons. The total organic content in these samples are found to range from several hundred parts-per-billion (ppb) to approximately twenty parts-per-million (ppm).

ABSTRACT

MOE'S VOLATILE ORGANIC MONITORING DEVELOPMENT PROGRAM

E. Singer, D. Toner, M. Sage, R. Corkum - Air Resources Branch, MOE

D. Corr, A. Szakolcai - Air Resources Branch, MOE

W. Offenbacher, G. Rees, J. Osborne - Lab Serv & Applied Research Br. MOE

G. Grosse - Southwestern Region, MOE

Although MOE possesses sophisticated mobile monitoring capability for organic vapours, these units cannot perform all of the large number of required surveys. Therefore a Volatile Organic Monitoring Development Program was established jointly by the Air Resources Branch, Laboratory Services and Applied Research Branch and the Regions of MOE. The objective of the program was to develop simple on-site sampling, off-site analytical methods for organic vapours.

Major milestones in the program included:

1. Cartridge development - Adsorbents;
2. Pump evaluation and sequential sampler development;
3. Standards generation;
4. Volatile organic preconcentrator development;
5. Analytical methodology development - Dual column chromatography with retention index identification/confirmation.
6. Determination of sample integrity - Effects of storage time and temperature;
7. Field testing.

The above developments and results are described. Further needs of the program are also highlighted.

A poster session manned by several of the collaborators will follow the presentation.

**THE INHALABLE PARTICULATE PROGRAM:
STUDIES OF AEROSOL DEPOSITION IN THE LUNG AND
POLLUTION SOURCE CHARACTERIZATION**

**John F. Hicks
Air Resources Branch**

Abstract

This presentation outlines the activities of the inhalable particulate program over the past two years. A brief synopsis of the dichotomous sampler - energy dispersive x-ray particulate analysis system used for a network of 11 Ontario sites introduces the presentation. Studies in particulate deposition and uptake in the body, and the source-receptor modelling of atmospheric aerosols constitute the main body of the talk. Finally, the dichotomous sampler - x-ray analysis system with source-receptor modelling is shown to have excellent possibilities of not only determining the degree of particulate pollution, but also which sources contribute the greatest amount and present the greatest risk to human health.

LASER INDUCED EMISSION SPECTROSCOPY OF PAHs
IN LOW TEMPERATURE MATRICES

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Abstract

Polynuclear Aromatic Hydrocarbons (PAH) are numerous, and sometimes nasty, constituents of our environment. Present analysis techniques are hard pressed to deal with the demands for identification and quantification. Emission spectroscopy in suitable normal alkane matrices at low temperatures can offer a complementary technique. A reference library of spectra, coupled with a "standards free" digital processing technique has been considered. Some of the pain involved in making the necessary transfer of technology is examined as well as the expected joys.

Provision of PAHs and Aza-PAHs as environmental analytical standards

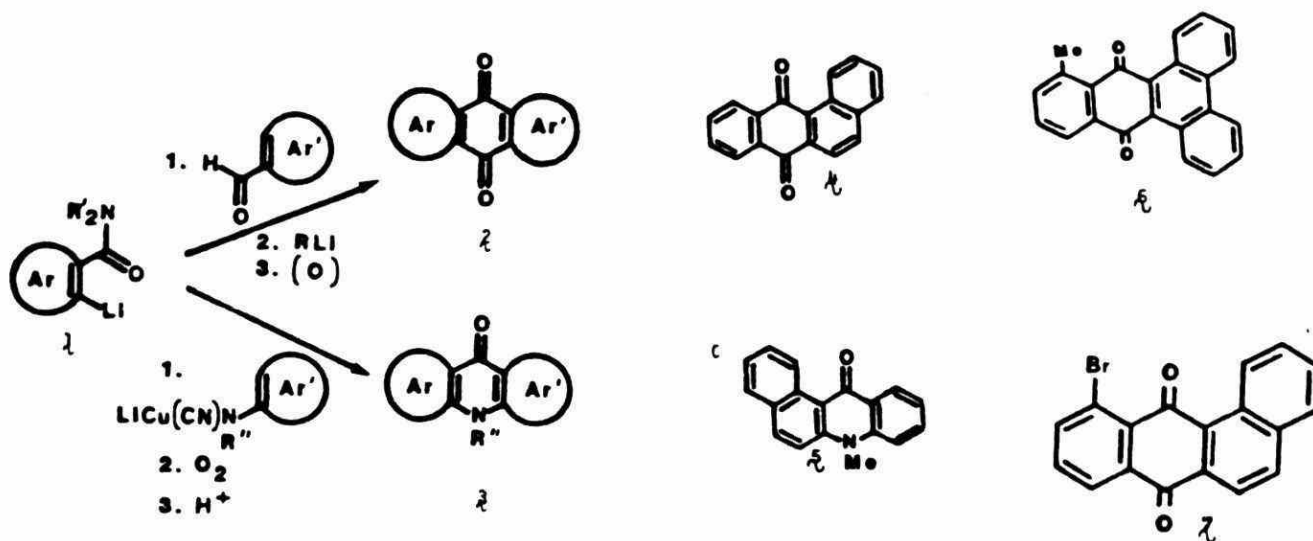
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ABSTRACT

The discovery of a tandem directed ortho metalation strategy (1 → 2) for the preparation of condensed aromatic substances in 1981 initiated a program in our laboratories aimed at providing a variety of PAHs and aza-PAHs of environmental interest. Using the directed metalation tactic, a variety of PAH-quinones (e.g. 4) and their corresponding PAHs were prepared by routes which were efficient, short, and involved minimum handling of toxic intermediates. By a new modification (1 → 3) the method was expanded to the preparation of aza-PAHs (e.g. the condensed acridine 5). The finding that silicon substitution may be used to protect reactive aromatic methyl groups allowed the regiospecific and general synthesis of methyl-substituted PAHs (e.g. 6). Conceptually similar methodology was derived from silicon protection of aromatic C-H sites which led to the synthesis of halo-substituted PAHs (e.g. 7).

All synthetic PAHs were purified by HPLC, characterized by high resolution NMR, and standardized by GC-MS methods. Over 20 compounds have been provided to the Ministry of the Environment for use in environmental research.



ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS AND THEIR DERIVATIVES IN ENVIRONMENTAL SAMPLES

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ABSTRACT

In recent years it has become clear from work with microbial mutagenesis assays and chemical fractionation techniques that there are many hazardous substances present in environmental samples that are still largely uncharacterized. Studies have shown that much of the mutagenic activity in urban airborne particulate extracts is associated with compound classes other than the PAHs and that much of the activity is of the "direct-acting" type. Several studies have shown that nitrated and oxygenated polycyclic aromatic hydrocarbons (nitro-PAHs and oxy-PAHs) are probably the principle direct-acting mutagens in automobile exhaust and urban air particulate samples. The environmental significance of these mutagens is not yet fully established, however, due in part to the lack of analytical methods for their determination and in part to the fact that many of these compounds may be formed as artifacts during the sampling step. Studies have shown that some PAHs can react readily with filter media, nitrogen oxides, sulfur oxides, ozone, and gas-phase photochemical smog to form a variety of derivatives. This paper will present some of the chromatographic and mass spectral methods that we have been developing for the analysis of PAHs and PAH derivatives and the results of our joint investigation with Concorde Scientific into new artifact-free methods of sampling.

A MASS SPECTROMETRIC STUDY OF SELECTED AIR POLLUTANTS

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ABSTRACT

Mass spectrometry is an extremely powerful tool not only for identification and quantification of polycyclic aromatic hydrocarbons (PAH), but also for reactivity, structure elucidation and investigation of ion chemistry, energetics and fragmentation behavior.

The results of mass spectrometric studies of reaction products of benzo(a)pyrene and chrysene with NO_2 and $^{15}\text{NO}_2$, as well as ion storage studies and reaction of benzo(a)pyrene with O_2 in ultraviolet light are presented.

In addition to conventional electron-impact mass spectra, mass-analyzed ion-kinetic-energy (MIKE) spectra can be obtained using a double-focusing mass-spectrometer in which the magnetic sector precedes the electric sector. Ions of a given species are selected by the magnetic sector and an appropriate fraction of those which are metastable undergo unimolecular dissociation in the second field-free region. The masses and translational energies of the resulting fragment ions are determined from energy spectra obtained by scanning the electric sector.

PAH offer a unique opportunity for the study of multiply-charged species since they readily form doubly- and triply- charged ions. The molecules themselves, and thus their fragments, are composed solely of carbon and hydrogen; charge separation studies of benzo(a)pyrene have led to an estimation of intercharge distances and charge locations within the molecule.

ABSTRACT

RETROSPECTIVE CORRELATION SPECTROSCOPY AND ITS APPLICATIONS TO
ATMOSPHERIC MONITORING.

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York University.

For environmental applications Retrospective Correlation Spectroscopy(RCS) uses the properties of the correlogram of a field spectrum, and a mask function (which represents the pollutant absorption features in the field spectrum) in a diagnostic fashion to infer concentrations and column densities of pollutants.

The work of the past year started with a numerical assessment of correlograms of the infrared spectrum of CO. This showed at once that it was essential to develop an detailed understanding of how the correlogram depends upon the characteristics of the field spectrum and of the mask.

Thus much effort has been devoted during the year to analytical and numerical studies of the properties of correlograms for model spectra and various masks. The model studies are applicable to the sulphur dioxide UV absorption spectrum.

The algebraic form for the correlation function which was developed in this work suggests a direct method for determination of column densities of pollutants.

Experiments are in progress to test this method and are discussed.

Development of a Tunable Diode Laser Based Hydrogen Peroxide Monitor

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ABSTRACT

Atmospheric gaseous hydrogen peroxide is formed mainly by the recombination of HO_2 radicals. Consequently, the measurement of its mixing ratio can be related to the mixing ratio of HO_2 and provide valuable insights into the chemistry of the odd hydrogen compound family in the troposphere. Also, hydrogen peroxide is believed to be the most important oxidant in the aqueous phase conversion of S(IV) to S(VI) in the troposphere.

A method for the real time determination of H_2O_2 in ambient air has been developed. It is based on tunable diode laser absorption spectroscopy in the 7.8 μm region. With a dual beam system and a multireflection cell pathlength of 40 m, 1-2 ppbv of H_2O_2 could be detected by scanning over a single absorption line every min. Spectra averaging over multiple scans and the subtraction of the background spectra improved the detection limits to 0.3-0.6 ppbv for a 15 min measurement time.

A permeation tube based system has been developed for the generation of gaseous calibration mixtures of H_2O_2 ranging from low ppbv to low ppmv mixing ratios. The effects of the transfer line materials and the linearity of the dilution of ppmv H_2O_2 mixtures down to the low ppbv range have been tested extensively.

Chemical Speciation of Airborne Particulate Matter

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Studies directed towards the determination of the chemical forms of elements present in airborne particulate material will be described. The reactions of vapours of fluorinated derivatives of 2,4-pentanedione with various elements and their compounds are being investigated. These reactions produce volatile metal complexes that can be used to collect the metal for determination. Several elements have been found to react and iron is under intensive study as a model element. Results obtained to date indicate that different compounds of iron react at different temperatures and that it should be possible to distinguish among these compounds on this basis.

Four approaches to trapping the volatilized material have been investigated. This study has shown that it should be possible to achieve separation of elements in the collection step in order to reduce interferences in the determination of the collected material.

As it is intended to employ neutron activation analysis (NAA) for the determination of collected elements, the automatic design of procedures in NAA is also being studied. A computer program based on mathematical modelling and simplex optimization has been created for the calculation of optimum analytical conditions. This technique can be used to formulate general guidelines for the application of NAA to airborne particulates and other materials. The combination of selective volatilization and properly-designed NAA is expected to lead to methods for the multielement speciation of airborne particulates.

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